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THERMAL PROPERTIES OF As-S GLASSES IN THE GLASS TRANSITION REGION

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The compositional dependence of T_g , C_p and relaxation enthalpy in the glassy system As-S was investigated. The observed modifications are related to the change of coordination polyhedra.

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Keywords: Chalcogenide glasses, Glass transition, Heat capacity, Configurational entropy

1. Introduction

Glass transition is usually characterized by a phenomenological value T_g and by a width of so-called glass transition region. In this region the diffusive motion of the melt begins to freeze in, before a glassy structure is achieved with viscosity values typical of solids 10^{14} Ns m⁻². Glasses are metastable solid materials without long range order. They lack translation and rotation symmetry. The nature of glass transition is complex and even today remains poorly understood. Numerous studies have been devoted to measurements and understanding of the glass transition temperature T_g which is influenced by experimental conditions. There is not consensus yet if structural or thermodynamic factor are responsible for determining of T_g .

2. Experimental

The glasses of the $As_xS_{(100-x)}$ system, where $x = 33 - 42$ at.%, were prepared by direct synthesis from the pure elements. The differential scanning calorimetry (DSC) experiments in the heating regime were performed using DSC Pyris 1 (Perkin-Elmer). The StepScan software (Perkin-Elmer) was used to separate steady state thermodynamic and kinetic processes in the glass transition region.

3. Results

Using the StepScan method the glass transition temperatures, T_g , were obtained. Main benefit of method used is ability to separate the heat capacity, C_p , representing the changes associated with the rapid molecular motion in the material in the time scale of experiment and enthalpy changes (thermodynamic component), ΔH_{T_g} , associated with slow irreversible processes (kinetic component) in the glass transition region. The quantities characterizing thermodynamic part of the glass transition are plotted in Fig.1. The dependencies of the specific heat capacity difference in the glass transition region, $\Delta C_{p,T_g}$, of the configurational entropy difference in the glass transition region, ΔS_{T_g} , and of the Gibbs free energy difference in the glass transition region, ΔG_{T_g} , on arsenic content were calculated from experimental DSC data.

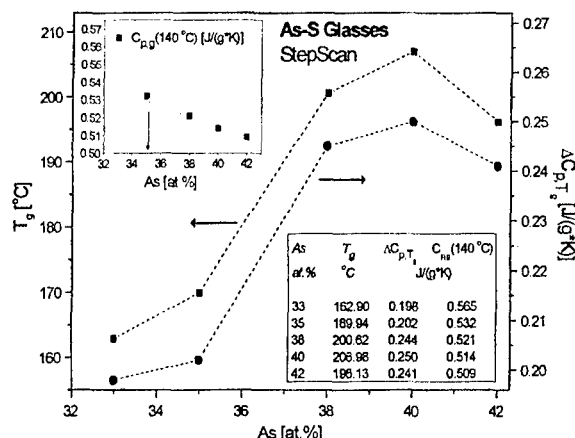


Fig. 1. The dependence of thermodynamic component of the glass transition (T_g , $\Delta C_{p,T_g}$) on arsenic concentration. In the insert: the compositional dependence of $C_{p,g}$ at the temperature 140 °C is shown. The curves are only for eye guidance.

The entropy difference in the glass transition region ΔS_{T_g} was calculated from the measured temperature dependence of C_p for all prepared glasses according to relation:

$$\Delta S = S_{T_1} - S_{T_2} = \int_{T_1}^{T_2} \frac{C_p}{T} dT, \quad (1)$$

temperature T_1 corresponds to the temperature of the beginning of the glass transition and T_2 temperature is the temperature of the melt at the end on the transformation. For result see Fig. 2.

Gibbs free energy difference in the glass transition region, ΔG_{T_g} , for all prepared samples was calculated:

$$\Delta G_{T_g} = \Delta H_{T_g} + T_{T_g} * \Delta S_{T_g}, \quad (2)$$

ΔH_{T_g} corresponds to so-called relaxation overshoot (the kinetic component). Gibbs free energy differences in the glass transition region, ΔG_{T_g} , for studied glasses are in Fig. 3. The strong discontinuity for glasses with 35–38 at.% of arsenic is found for both dependencies.

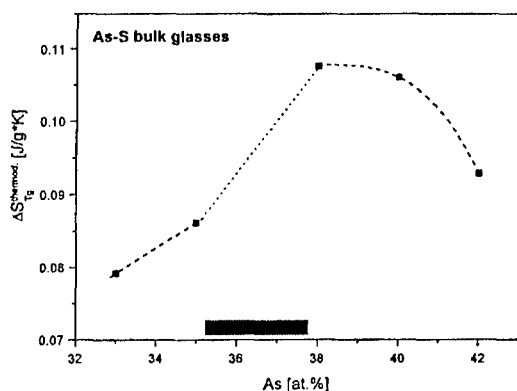


Fig. 2. The dependence of the configuration entropy difference, ΔS_{T_g} , in the glass transition region on the arsenic content.

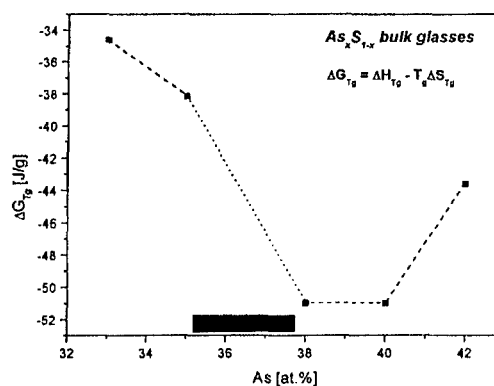


Fig. 3. The dependence of Gibbs free energy difference in the glass transition region ΔG_{T_g} on the concentration of arsenic.

Similarly strong change was observed by Borisova [1] for composition dependence of the thermal expansion coefficient α , see Fig. 4.

All results obtained were also plotted as functions of the mean coordination number $\langle r \rangle$, Fig. 5.

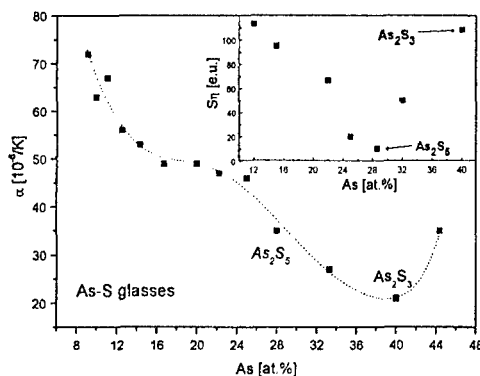


Fig. 4. The temperature dependence of the thermal expansion coefficient α on the concentration of arsenic. Inset shows the dependence of viscous-flow activation entropy on arsenic content [1].

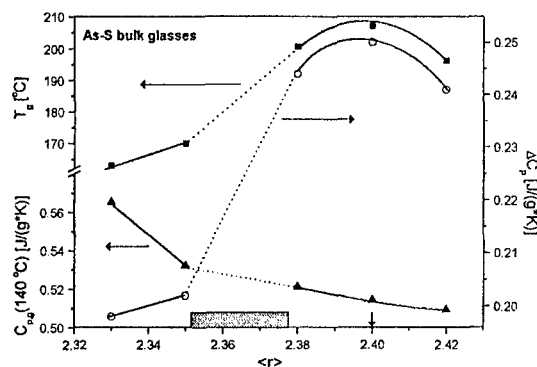


Fig. 5. The dependence of obtained thermodynamic quantities in the glass transition region as function of $\langle r \rangle$ for 3-fold arsenic.

4. Discussion

The glass transition temperatures were determined from measured $C_p(T)$ dependencies, Fig. 1. It was found that T_g reaches maximal value for stoichiometric composition As_2S_3 . The calculated dependence of the heat capacity difference at T_g , $\Delta C_{p,T_g}$, reaches maximum for As_2S_3 as well as in the case of As-Se glasses, see [2]. The concentrational dependence of $C_{p,g}$ at 140 °C, i.e. at temperature lower than onset of the glass transformation temperature, is shown in the inset into Fig. 1. It is obvious that for chemical compositions close to $As_{35}S_{65}$ the strong change of the slope of dependence of $C_{p,g}$ on As concentration takes place. From the compositional dependence of the configuration entropy difference, ΔS_{T_g} , in the glass transition region (Fig. 2) it is possible to conclude that the change of the basic structural units probably takes place in the studied glasses.

Borisova [1] supposes for 28.57 at.% of arsenic existence of quasi-tetrahedral units which correspond to As_2S_5 glass composition, and pyramidal units $AsS_{3/2}$ for the stoichiometric As_2S_3 composition. In the region between these two limit compositions the transformation of quasi-tetrahedral units into pyramidal units takes place, a vice versa. On going from As_2S_5 to As_2S_3 the value of viscous-flow activation entropy S_η increases which represents, according to [1], a transition from tetrahedral to trigonal coordination of arsenic in As-S glasses (see Fig. 4, inset). Studied glasses predominantly fall in this transformation region. X-ray and neutron diffraction measurements shown that structure of As-S and As-Se glasses are very similar in the range of compositions $x = 0 - 70$, [3]. On the base of changes of T_g slope on concentration of arsenic it is concluded [4] that two fractions of chemical composition could coexist in this region of chemical compositions. Authors [4] suppose that two possible oxidation states of arsenic can exist in the studied covalent glasses, i.e. As^V and As^{III} . One fraction of the above mentioned glasses can be created by 4-fold coordinated As^V with quasi-tetrahedral local configuration with three bridging Se atoms and one double bonded Se. In the second one there are preliminary units with 3-fold coordinated As^{III} in pyramidal configuration. The change of $C_{p,g}$ slope on composition for $x = 35$ at.% As was observed, see Fig. 1, inset. We suppose structural units changing close this composition. Providing that all arsenic is 3-fold coordinated (As^{III}) the mean coordination number $\langle r \rangle = 2.35$. If all arsenic is 4-fold coordinated (As^V) the mean coordination number $\langle r \rangle$ would be 2.7. It is necessary to point out that these two limited values are very close to the values for so-called chemical and/or topological transitions i.e. $\langle r \rangle = 2.4$ or 2.65 [5,6]. According to the constraint theory it is suggested [5] that valence forces (bond-stretching and bond-bending) can serve as the atomic constraints in the covalent network. It is supposed that glass formation would be optimal (ideal mechanical stability) when the number of constraints per atom equals 3 (3 degrees of

freedom per atom in 3D network). These ideas lead to the recognition that glass network becomes for $\langle r \rangle = 2.4$ elastically rigid. The rigid clusters can percolate and a phase transition (so-called rigidity transition) can take place. The feature observed at $\langle r \rangle = 2.67$ was understood using the structural transition model as well [6]. It was established by topological consideration using medium-range structures and it is attributed to the transition from essentially layered structure to 3D network arrangement due to the cross-linking. The dependence of obtained thermodynamic quantities in the glass transition region as function of $\langle r \rangle$ is shown in Fig. 5. There are shown studied dependencies for the case when only pyramidal structural units are present in the glasses. Strong discontinuities are evident again. Pyramids are also supposed to be main structural units in As-Se glasses with $x \leq 40$ at.% As, [7].

It is not possible to prepare crystalline analogs of As-S glasses, except of As_2S_3 [8] and so it is necessary to bear on indirect data only for their analysis, unfortunately.

5. Conclusions

Compositional dependence for $\text{As}_x\text{S}_{(100-x)}$ ($x = 33 - 42$ at.% As) of T_g , C_p and relaxation enthalpy in the glass transition region were measured. Obtained data show that the changes of oxidation state and associated changes of the coordination number of arsenic take place very probably in the studied region of chemical compositions. Changes in the studied quantities reflect the changes of coordination polyhedra (short-range order change). Observed changes are in good agreement with published structural studies dealing with the above mentioned glasses.

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